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(71) 出願人 035003159
 東レ株式会社
 東京都中央区日本橋室町2丁目2番1号
 (72) 発明者 酒井 良忠
 滋賀県大津市園山1丁目1番1号 東レ株式会社滋賀事業場内
 (72) 発明者 島垣 昌明
 滋賀県大津市園山1丁目1番1号 東レ株式会社滋賀事業場内
 (72) 発明者 田中 和実
 滋賀県大津市園山1丁目1番1号 東レ株式会社滋賀事業場内

(54) 【発明の名称】 親水化膜およびその製造法

(57) 【要約】

【課題】 溶出性成分を伴わずに、ポリスルホン膜を用いた親水化膜を提供する。

【解決手段】 (1) ポリスルホンを主体とした疎水性成分と、物理的に不溶化したポリビニルピロリドンとからなる親水化膜。

(2) ポリスルホンを主体とした疎水性高分子を主たる素材とした膜の製造工程中でビニルピロリドンを導入し該ビニルピロリドンを放射線または／および熱により水不溶化することを特徴とする親水化膜の製造法。

【特許請求の範囲】

【請求項 1】ポリスルホンを主体とした疎水性成分と、物理的に不溶化したポリビニルピロリドンとからなる親水化膜。

【請求項 2】親水化膜が、中空糸膜であることを特徴とする請求項 1 記載の親水化膜。

【請求項 3】ポリスルホンを主体とした疎水性高分子を主たる素材とした膜の製造工程中でビニルピロリドンを導入し該ビニルピロリドンを放射線または／および熱により水不溶化することを特徴とする親水化膜の製造法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、新規な親水化膜およびその製造法に関する。

【0002】

【従来の技術】従来、濾過処理や透析処理で用いられる水処理用膜は、(1) グリセリンなどの水溶性膜透過能維持剤を用いた状態、(2) 膜素材として親水性高分子を用いた状態、(3) 水を共存させた状態、などで供給されてきた。しかし、(1) では使用に先立って膜透過能維持剤を洗浄除去する必要がある、即時使用ができないこと、(2) では一般にポアサイズが小さくなり、分子量数万以上の成分の分離に使える膜ができにくいこと、(3) では被処理液体が血液である場合など、共存している水を予め被処理液体に変質を与えない液体に置換する必要がある用途があり、即時使用できないことなど、それぞれに問題がある。

【0003】一方、膜素材として、ポリエチレン、ポリプロピレン、ポリカーボネート、ポリアクリロニトリル、ポリスルホン、ポリエステル、ポリ 2 弗化ビニリデン、ポリ 4 弗化エチレン、ポリメチルメタクリレート、セルローストリアセテートなどの疎水性高分子を主たる素材とした膜が濾過膜や透析膜として提供されているが、これらの疎水性膜では(1) や(3) の状態にしておかないと直ちには本来の透過能を発揮できず、したがって前記のように即時使用できない問題は疎水性膜の宿命とされてきた。また、疎水性膜に対して親水性成分を導入し、固着させることで即時使用を可能にするという例（例えば、特開昭 61-120602、特開昭 61-125405、特開昭 61-125408、特開昭 61-125409、特開昭 61-133102、特開昭 61-133105 など）もみられるが、これらでは親水性高分子の固着が不十分で、使用中に膜から親水性成分が溶出してくるなどの問題がある。

【0004】

【発明が解決しようとする課題】本発明者らは、かかる状況に鑑み、溶出性成分を伴わずに疎水性膜を即時使えるようにするには如何にすべきかにつき鋭意検討を重ねたところ本発明に到達した。

【0005】

【課題を解決するための手段】即ち、本発明は、上記目的を達成するために下記の構成を有する。

【0006】「(1) ポリスルホンを主体とした疎水性成分と、物理的に不溶化したポリビニルピロリドンとからなる親水化膜。

【0007】(2) ポリスルホンを主体とした疎水性高分子を主たる素材とした膜の製造工程中でビニルピロリドンを導入し該ビニルピロリドンを放射線または／および熱により水不溶化することを特徴とする親水化膜の製造法。」

【0008】

【発明の実施の形態】本手段を適用できる疎水性膜素材としては特に限定するものではないが、ポリエチレン、ポリプロピレン、ポリカーボネート、ポリアクリロニトリル、ポリスルホン、ポリエステル、ポリ 2 弗化ビニリデン、ポリ 4 弗化エチレン、ポリメチルメタクリレート、セルローストリアセテート、ポリスチレン、ポリエチルアクリレート、ポリ酢酸ビニル、ポリ塩化ビニルなど、およびこれらの誘導体、あるいはこれら重合体の構成単量体間の共重合体、さらにはこれらを主体とするが共重合成分として親水性成分を少量含む重合体などが挙げられ、本手段は平衡吸水率（20℃、相対湿度 65% の雰囲気下に 1 週間置いて測定した吸水率で、水重量／ポリマー重量を％で表示した値）が 5% 以下、さらに望ましくは 2% 以下の素材に適用できる。

【0009】親水性高分子の水不溶化手段として放射線を照射する方法と加熱する方法とがあるが、前者ではポリエチレン、ポリスルホン、ポリスチレン、ポリエステル、ポリエチルアクリレート、ポリ酢酸ビニルなどを主成分とする耐放射線性に優れた素材に対して、後者ではポリカーボネート、ポリスルホン、ポリ 2 弗化ビニリデン、ポリ 4 弗化エチレン、ポリエステルなどを主成分とする耐熱性に優れた素材に対して好適に用いられる。またさらに、ポリスルホン、ポリエステルなどのように耐放射線性および耐熱性に共に優れた素材に対しては、両手段を併用することも可能である。

【0010】放射線により水不溶化する親水性成分としては、ビニルピロリドン、ヒドロキシエチルメタクリレート、ビニルアルコール、エチレングリコール、メトキシポリエチレングリコールメタクリレートなど、およびこれらの誘導体のモノマー、オリゴマー、ポリマーおよびこれらの間のコポリマー、あるいはペプタイド、アルブミン、コラーゲンなどの蛋白などが挙げられる。熱により水不溶化する親水性成分としては、ビニルピロリドン、ε-カプロラクタム、ビニルアルコール、エチレンオキシド、ヒドロキシエチルメタクリレートなど、およびこれらの誘導体のモノマー、オリゴマー、ポリマー、およびこれらの間のコポリマー、あるいはペプタイド、アルブミン、コラーゲンなどの蛋白などが挙げられる。

【0011】水不溶化手段としての放射線としては、ガンマー線、紫外線、電子線などが用いられるが、特にガンマー線では浸透性が高いので単一膜だけでなく、膜集合体や膜を組込んだモジュール状態でも親水性成分の水不溶化処理が行なえるので好適に用いられる。水不溶化手段としての加熱手段としては、乾熱、湿熱、温浴加熱のいずれも用いることができる。加熱温度としては、疎水性素材の軟化点や融点、親水性成分の熱分解温度などを考慮する必要があるが、50℃ないし200℃が好ましい。また、加熱処理を親水性成分を水不溶化する手段としてだけでなく、ポアサイズの調整手段も兼ね合せた手段として用いることも可能である。親水性成分を導入する製膜段階としては、膜素材へのブロック共重合体化、製膜原液への混入、疎水性膜製膜後の後処理など、いずれの段階でも良いが、製膜原液への混入や後処理による導入が大きな孔を確保しやすいという点、親水性成分の使用量を削減できるという点などで有利である。また、放射線照射や加熱処理を膜や膜を組込んだモジュールの殺菌手段を兼ねたものとすることも可能である。

【0012】本発明でいう膜の形態は特に限定するものではなく、例えばシート状、中空糸状、マイクロカプセル状の膜などが挙げられる。

【0013】

【実施例】以下、本発明の有効性を実施例をもって説明する。そこで用いた測定法は次の通りである。

【0014】(1) 透水性

中空糸膜の場合は、両端に環流液用の孔を備えたガラス製のケースに該中空糸膜を挿入し、市販のポッティング剤を用いて小型モジュールを作製し、37℃に保って中空糸内側に水圧をかけ膜を通して外側へ透過する一定時*30

*間の水の量と有効膜面積および膜間圧力差から算出する方法で透水性能を測定した。

【0015】(2) 溶出物

膜0.5gを70℃温水50ccで1時間加熱して試験液を調製する。試験液の波長220～350μmにおける吸光度を測定する。なお、透析型人工腎臓装置承認基準では、本条件での規格を0.1以下としている。

【0016】実施例1

ポリスルホン(アモコ社 Udel-P3500)18部、ポリビニルピロリドン(BASFK30)10部をジメチルアセトアミド71部、水1部に加え、90℃10時間加熱溶解し、製膜原液とした。この原液を外径0.3mm、内径0.2mmの2重環状口金から芯液としてジメチルアセトアミド65部、水35部からなる溶液を吐出させ、乾式長350mm、~~相対湿度85%~~85%中を通し、40℃の20%のジメチルアセトアミド水溶液中に導き、中空糸膜を製膜した。この中空糸膜を1.6m²になるように、ケースに充填し、ポッティングしてモジュールとした。湿潤状態でγ線照射後、透析型人工腎臓装置承認基準の溶出物試験の紫外吸収スペクトルを測定したところ0.1以下であった。本中空糸は、走査型電子顕微鏡で膜孔径を測ったところ、120Å程度であって透析処理用途に用いることができる。

【0017】比較例1

γ線照射を省いた点を除いて、実施例1をくり返し、乾燥後、透水性能の測定をしたところ実質上ゼロであった。

【0018】

【発明の効果】本発明により、溶出性成分を伴わずに、ポリスルホン膜を用いた親水化膜を提供することができた。

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(71)Applicant : TORAY IND INC

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(72)Inventor : SAKAI YOSHITADA
SHIMAGAKI MASAOKI
TANAKA KAZUSANE

(54) HYDROPHILIC MEMBRANE AND ITS PRODUCTION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a hydrophilic membrane using a polysulfone membrane without being accompanied by a component having elution properties.

SOLUTION: A hydrophilic membrane consists of a hydrophobic component based on polysulfone and physically insolubilized polyvinyl pyrrolidone and is produced by introducing vinyl pyrrolidone during a process manufacturing a membrane by using a hydrophobic polymer based on polysulfone as a main material and making the same water-insoluble by radiation and/or heat.

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CLAIMS

[Claim(s)]

[Claim 1] Hydrophilization film which consists of a hydrophobic component which made polysulfone the subject, and a polyvinyl pyrrolidone which insolubilized physically.

[Claim 2] Hydrophilization film according to claim 1 with which the hydrophilization film is characterized by being a hollow fiber.

[Claim 3] The manufacturing method of the hydrophilization film characterized by introducing vinyl pyrrolidone in the production process of the film which used the hydrophobic giant molecule which made polysulfone the subject as main material, and carrying out water insolubilization of this vinyl pyrrolidone with a radiation or/and heat.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the new hydrophilization film and its manufacturing method.

[0002]

[Description of the Prior Art] The film for water treatment conventionally used by filtration processing or dialysis processing is (1). The condition and (2) using water-soluble film penetrability maintenance agents, such as a glycerol, A condition and (3) using the hydrophilic macromolecule as a film material It has been supplied in the condition of having made water living together etc. However, (1) It is necessary to carry out washing removal of the film penetrability maintenance agent then in advance of use, and use is impossible instantly, (2) The film which can be used for separation of a 10,000 or more molecular weight numbers component by then generally pore size becoming small cannot be made easily, (3) When a treated liquid is blood then, there is an application which needs to permute the water which lives together by the liquid which does not give deterioration beforehand to a treated liquid, and that it cannot be used instantly etc. has a problem in each.

[0003] On the other hand, as a film material, polyethylene, polypropylene, a polycarbonate, Although the film which used hydrophobic macromolecules, such as a polyacrylonitrile, polysulfone, polyester, Pori 2 fluoridation vinylidene, Pori 4 fluoridation ethylene, polymethylmethacrylate, and cellulose triacetate, as main material is offered as a filtration membrane or permeable membrane With these hydrophobic film, it is (1). (3) The problem which cannot demonstrate the penetrability of ***** shortly after not changing into a condition, therefore cannot be used instantly as mentioned above has been made into the fate of the hydrophobic film. Moreover, a hydrophilic component is introduced to the hydrophobic film, although the examples (for example, JP,61-120602,A, JP,61-125405,A, JP,61-125408,A, JP,61-125409,A, JP,61-133102,A, JP,61-133105,A, etc.) which say [which it is made possible] use instantly by making it fix are also seen, these of fixing of a hydrophilic macromolecule are insufficient, and there is a problem of a hydrophilic component being eluted from the film while in use.

[0004]

[Problem(s) to be Solved by the Invention] When this invention persons took lessons from how it should carry out in view of this situation for enabling it to use the hydrophobic film instantly, without being accompanied by the elution nature component and piled up examination wholeheartedly, they reached this invention.

[0005]

[Means for Solving the Problem] That is, this invention has the following configuration, in order to attain the above-mentioned purpose.

[0006] "Hydrophilization film which consists of a hydrophobic component which made (1) polysulfone the subject, and a polyvinyl pyrrolidone which insolubilized physically.

[0007] (2) Manufacturing method of the hydrophilization film characterized by introducing vinyl pyrrolidone in the production process of the film which used the hydrophobic giant molecule

which made polysulfone the subject as main material, and carrying out water insolubilization of this vinyl pyrrolidone with a radiation or/and heat. "

[0008]

[Embodiment of the Invention] Although it does not limit especially as a hydrophobic film material which can apply this means Polyethylene, polypropylene, a polycarbonate, a polyacrylonitrile, Polysulfone, polyester, Pori 2 fluoridation vinylidene, Pori 4 fluoridation ethylene, Polymethylmethacrylate, cellulose triacetate, polystyrene, These derivatives, such as polyethylacrylate, polyvinyl acetate, and a polyvinyl chloride, Or although these are made into a subject at the copolymer between the configuration monomers of these polymers, and a pan, a little **** polymer etc. is mentioned in a hydrophilic component as a copolymerization component. Balanced water absorption (value which is the water absorption which placed for one week and was measured, and displayed water weight / polymer weight by % on the bottom of 20 degrees C and the ambient atmosphere of 65% of relative humidity) can apply this means to 2% or less of material still more desirably 5% or less.

[0009] Although there are an approach of irradiating a radiation as a water insolubilization means of a hydrophilic macromolecule and the approach of heating, at the former, it is suitably used to the material excellent in the thermal resistance which uses a polycarbonate, polysulfone, Pori 2 fluoridation vinylidene, Pori 4 fluoridation ethylene, polyester, etc. as a principal component to the material excellent in the radiation resistance which uses polyethylene, polysulfone, polystyrene, polyester, polyethylacrylate, polyvinyl acetate, etc. as a principal component by the latter. Furthermore, it is also possible to use a both-hands stage together to polysulfone and the material which was excellent in both radiation resistance and thermal resistance like polyester.

[0010] As a hydrophilic component which carries out water insolubilization with a radiation, proteins, such as the monomer of these derivatives, such as vinyl pyrrolidone, hydroxyethyl methacrylate, vinyl alcohol, ethylene glycol, and methoxy polyethylene-glycol methacrylate, oligomer, a polymer and a copolymer between these or peptide, albumin, and a collagen, etc. are mentioned. As a hydrophilic component which carries out water insolubilization with heat, proteins, such as the monomer of these derivatives and oligomer, such as vinyl pyrrolidone, epsilon caprolactam, vinyl alcohol, ethyleneoxide, and hydroxyethyl methacrylate, a polymer and a copolymer between these or peptide, albumin, and a collagen, etc. are mentioned.

[0011] As a radiation as a water insolubilization means, although a gamma ray, ultraviolet rays, an electron ray, etc. are used, since water insolubilization processing of a hydrophilic component can be performed also in the state of the module which incorporated not only simple gland but a film aggregate, and the film since permeability was especially high by the gamma ray, it is used suitably. As a heating means as a water insolubilization means, both dry heat wet heat and hot bath heating can be used. As whenever [stoving temperature], although it is necessary to take into consideration the softening temperature of a hydrophobic material, the melting point, the pyrolysis temperature of a hydrophilic component, etc., 50 degrees C thru/or 200 degrees C are desirable. Moreover, it is possible it not only to make heat-treatment into the means which carries out water insolubilization of the hydrophilic component, but to use as a means which served also as the adjustment device of pore size. As a film production phase which introduces a hydrophilic component, although which phase is available for block-copolymer-izing to a film material, mixing to a film production undiluted solution, the after treatment after hydrophobic film film production, etc., it is advantageous at the point of being easy to secure a hole with big mixing to a film production undiluted solution and installation by after treatment, the point that the amount of the hydrophilic component used is reducible, etc. Moreover, it is also possible to have served as the sterilization means of the module which incorporated the film and the film for radiation irradiation or heat-treatment.

[0012] Especially the gestalt of the film as used in the field of this invention is not limited, and the film of the shape of the shape of the shape of a sheet and a hollow filament and a microcapsule etc. is mentioned.

[0013]

[Example] Hereafter, the effectiveness of this invention is explained with an example. Then, the used measuring method is as follows.

[0014] (1) In the case of the permeable hollow fiber, this hollow fiber was inserted in the glass case which equipped both ends with the hole for ring current liquid, it produced the small module using the commercial potting agent, and measured permeable ability by the approach of compute from the amount of the water of fixed time amount which keeps at 37 degrees C, pours water pressure on the hollow filament inside, and is penetrated outside through the film, an effective film surface product, and the differential pressure between film.

[0015] (2) Heat 0.5g of effluent film with 50 cc of 70-degree-C warm water for 1 hour, and prepare test fluid. The absorbance in the wavelength of 220-350 micrometers of test fluid is measured. In addition, specification in these conditions is made or less into 0.1 on dialysis mold hemodialysis apparatus acknowledgement criteria.

[0016] It is dimethylacetamide 71 about the example 1 polysulfone (Amoco Corp. Udel-P3500) 18 section and the polyvinyl-pyrrolidone (BASFK30) 10 section. In addition to the section and the water 1 section, the heating dissolution was carried out for 90-degree-C 10 hours, and it considered as the film production undiluted solution. this undiluted solution -- the outer diameter of 0.3mm, and bore of 0.2mm a duplex -- annular -- the solution which consists of the dimethylacetamide 65 section and the water 35 section as core liquid was made to breathe out from a mouthpiece, the inside of 350mm of dry type length and 85% of relative humidity was drawn into through and 20% of 40-degree C dimethylacetamide water solution, and the hollow fiber was produced. It is this hollow fiber 1.6m 2 Potting was filled up and carried out to the case and it considered as the module so that it might become. When the ultraviolet absorption spectrum of the eluting material test of a dialysis mold hemodialysis apparatus acknowledgement standard was measured after gamma irradiation by the damp or wet condition, it was 0.1 or less. When this hollow filament measures a film aperture with a scanning electron microscope, it is about 120A and can be used for a dialysis processing application.

[0017] When the example 1 was repeated and measurement of permeable ability was carried out after desiccation except for the point of having excluded example of comparison 1 gamma irradiation, it was parenchyma top zero.

[0018]

[Effect of the Invention] The hydrophilization film using the polysulfone film was able to be offered by this invention, without being accompanied by the elution nature component.

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